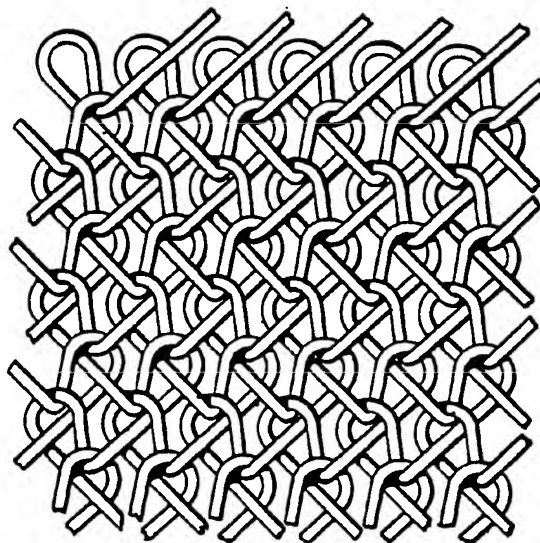




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(54) Title: IMPROVEMENTS IN OR RELATING TO CATALYSTS AND GETTER SYSTEMS

**(57) Abstract**

Knitted precious metal textiles such as wire gauzes, and methods of making the same, are disclosed. The textiles are suitable for use in catalysis, and are especially useful for the catalytic processing of ammonia. Particularly preferred knitting stitches are tricot, jacquard and raschel. Rotary or circular knitting machines may be used, but warp knitting machines are preferred for most applications. Advantageous products produced by the knitting process are described. These products include layers of non-uniform thickness, and uncut products having non-parallel side edges, such as circles.

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IMPROVEMENTS IN OR RELATING TO
CATALYSTS AND GETTER SYSTEMS

This invention relates to catalysts and to getter systems for catalysts. The invention relates particularly, though not
5 exclusively, to catalysts and getter systems that are suitable for ammonia oxidation systems. Examples are catalysts used in the production of nitric acid, hydrocyanic acid and other ammonia oxidation products.

The oxidation of ammonia (NH_3) to form other useful products,
10 such as nitric acid (HNO_3) or hydrogen cyanide (HCN), is generally effected, in industry, by a catalytic process. This process involves one or more precious metal oxidation catalysts. The most widely used catalyst is platinum, either alone or in combination with other platinum group metals, such
15 as rhodium and palladium.

For much of this century, catalysts for reactions such as the oxidation of ammonia have been in the form of woven gauze of, for example, a platinum group metal (pgm) alloy. Getter systems for catalysts also rely upon woven gauze. The gauze
20 is usually made up of wires, but other elongate elements such as strips may also be used; in this specification, the term 'wire' is intended to encompass such other elongate elements.

Typically, in use in a reactor chamber, the wire gauze is supported in the path of reacting gases or fluids, which flow
25 thorough the gauze and contact the catalytic material under controlled conditions.

Weaving of catalytic gauzes is commonly performed on a loom, in a process very similar to the weaving of textile cloths, i.e. with individual warp and weft strands of wire. The mesh
30 thereby obtained is usually regular, with rectangular (normally square) interstices. Variants to this plain weave

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include herringbone or twilled weave. The nature of the weaving process also means that the gauze itself is rectangular in shape when it comes off the loom.

Modern gauzes commonly feature 80 meshes per square inch (1024
5 per cm^2), using 0.003 inch diameter wire (0.076 mm). Other wire diameters in common use are 0.0024 inches (0.060 mm), 0.0027 inches (0.085 mm), 0.0036 inches (0.090 mm), and 0.1 mm.

The thickness of the wire and the size of the mesh is
10 important, because the reaction gases must pass through the wire gauze at a reasonably rapid rate that is consistent with the efficiency of the catalyst, but without excessive back pressure. The wire thickness is significant in two respects:
15 firstly, the thicker a wire, the larger its surface area and secondly, the thicker a wire, the longer it can last under conditions of volatilisation (evaporation).

Bearing in mind that the oxidation of ammonia is a heat-intensive process involving an exothermic reaction, the gauze must be able to withstand the stress of very high temperature
20 and flowing reactive gases without excessive degradation, and without excessive loss of catalytic or reaction efficiency.

Known, woven gauzes suffer from a number of disadvantages. Weaving is a slow process even if relatively fast 'rapier' or 'projectile' looms are used. This results in production
25 delays, and represents a high production cost in terms of area of catalytic gauze produced per hour. Also, where the gauze is made of precious metals and is therefore of substantial value, the slowness of weaving ties up expensive capital assets for an undesirably long period of time. This
30 phenomenon, known as "metal lockup", means that large reserves of precious metal lay idle, and are isolated from world markets at great expense, while awaiting processing into woven gauzes.

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The slowness of weaving is made all the worse by the need for laborious setting-up procedures whenever a new gauze is to be produced, or even when a wire of different composition or diameter is to be introduced into the gauze. It is also
5 difficult to vary wire density. In short, the weaving process lacks flexibility.

Woven gauzes themselves suffer from problems. For example, because woven gauzes are generally of rectangular shape when produced, they must be woven 'over size' and then cut down if
10 the desired final shape is circular or otherwise non-rectangular. The offcuts constitute scrap and, consequently, represent undesirable waste. The cutting process adds further production time.

Woven gauze is also prone to warp under thermal stress during
15 exothermic reactions, forming a tortoise-shell pattern of creases, ridges or wrinkles. These ridges can cause undesirable side reactions in some processes. In hydrogen cyanide reactors, for example, they can give rise to carbon deposits because the effective bed depth, and hence residence
20 time of reaction gases and by-products, is increased at the site of the ridges. Carbon may then be deposited on the surface of the catalyst, thus obscuring the catalytic surface much to the detriment of catalytic efficiency. The carbon can even combine with the catalytic material, causing
25 embrittlement and thus increasing the risk of mechanical failure. In nitric acid reactors such ridges also cause local areas of greater effective catalytic depth resulting in different rates of reaction and efficiency.

The layers in a catalyst pack may also weld together by
30 diffusion welding at the site of any ridges, further limiting catalytic efficiency due to reduced surface area. Welding also restricts the freedom of movement of the layers with respect to one another, further worsening the wrinkling problem.

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Woven gauzes also suffer from an uneven distribution of mechanical strength throughout the gauze, which is an inherent consequence of the weaving process and its use of perpendicular warp and weft wires. Woven gauzes are also known to experience stress failure in the reactor, due to the pressures of flowing gases. Thermal expansion of the gauze in the reactor also can lead to serious problems. Conventional gauzes deteriorate at the high temperatures of many industrial oxidation reactions.

10 Precious metal gauzes continue to flourish despite their disadvantages, because of their relative simplicity and ease of manufacture, and because they are well known as reliable, reasonably efficient, and reasonably economic industrial catalysts. Nonetheless, efforts to find improved catalysts and catalyst supports continue, with the work of practitioners focused not so much on substitutes or replacements for precious metal gauzes, but on new catalyst support materials that are not made of precious metal, and which are designed to be used in combination with conventional precious metal gauzes, or with other known catalysts. These supports are intended to relieve some of the stresses on conventional gauzes, and purport to improve reaction efficiency in some cases.

It is against this background that the present invention has been devised. In a broad sense, the invention resides in the concept of producing precious metal gauzes by a knitting process. The invention also resides in knitted precious metal gauzes per se. Thus, the present invention provides knitted precious metal textiles that are useful as catalysts and/or as getter materials for catalyst recovery. These knitted metal textiles are particularly useful in ammonia oxidation processes, such as the production of HNO_3 or HCN .

Knitting machines are generally much quicker than looms in terms of area of gauze produced per hour, once in steady

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production. Knitted precious metal textiles can be made as much as ten times faster than metal gauzes can be woven by conventional methods. Thus, the present invention increases the speed at which catalyst and getter materials can be produced. In this way, the knitting process of the invention, and the resulting knitted textile products, overcome or at least mitigate the economic disadvantages of weaving, and in particular obviate problems of metal lockup and the high investment costs traditionally associated with the production of precious metal catalyst and getter gauzes.

Not only is knitting a faster process than weaving, but knitting machines can be set up and put into production much more quickly than looms. In other words, the set-up time for knitting wires into textiles is much shorter than the set-up time of the looms needed to weave metal gauzes. This reduces equipment and start-up costs for the production of catalysts and getter systems.

A further advantage of the invention is that, in general, knitting machines are much more flexible than looms, being able to cater readily for changes in the constituent wires simply by changing the wires that are fed to the knitting machine. Unlike a loom, which must be tediously rethreaded over a large area when wires are changed, a knitting machine need only be supplied with the new wire instead of the old wire. Similarly, different wires (e.g. of different alloys or diameters) can be much more readily combined in one final knitted textile than can easily be combined on a weaving loom.

In general, knitting machines are able readily to produce gauzes of varying characteristics. In particular, knitting machines can produce gauzes of varying shapes such as circles and hexagons, thereby minimising offcut scrap which currently can approach 25% of the gross woven area.

It is also possible substantially to increase the wire density

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of the gauze simply by feeding two or more wires into the knitting machine in parallel. Knitting permits the use of more and thinner wires in a knitted textile, in comparison with a woven gauze. By means of the invention, one, two, or more
5 strands of wire can be knitted simultaneously. Thus, the density of the knit and the number of wires can be controlled and changed in production. This is particularly advantageous in getter systems, which often use more and thinner wires than catalyst systems. These kinds of adjustments during production
10 are much more difficult if not impossible when weaving a gauze on a loom.

The invention also allows the interstices in the textile to be of different shapes, depending on the knitting stitch. Conventional weaving provides rectangular (square or oblong)
15 interstices, which limits the effective catalytic or getter surface area in comparison with the shapes and flow patterns that can be provided by using different knitting stitches. The knots created by knitting also provide increased wire density per volume, in comparison with woven goods that do not have
20 knots. This can also provide increased catalyst or getter surface areas for a given apparent area.

A further advantage of knitting is that the resulting gauze is typically more open and flexible or pliable than a corresponding woven gauze, while being more resistant to
25 breakage under stress. As a result of this flexibility, a knitted gauze is less likely than a woven gauze to warp into ridges under thermal stress. In particular, the textiles of the invention have a close knit structure, rather than a conventional loose weave, and can more readily accommodate
30 thermal expansion without forming the tortoise shell ridges that are often seen in woven gauzes. This reduces the problem of side reactions and carbon build up observed in HCN reactors that use conventional woven gauze.

The surprising advantages of knitted textiles in high-

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temperature environments are emphasised by the very high temperatures that prevail in hydrogen cyanide (HCN) production, in which HCN is synthesised from ammonia and methane in the 'Andrussow' process. Thus, a specific aspect of this invention relates to the use of a knitted textile as a catalyst in the synthesis of hydrogen cyanide from ammonia and methane.

The invention provides knitted textiles made from precious metals and alloys thereof (referred to in this specification simply as 'precious metals'). In particular, wires of platinum, rhodium, palladium and combinations thereof can be used, in proportions known to be useful for catalyst or getter applications. Whilst the invention contemplates any knitting stitch, wire textiles produced on a rotary knitting machine or a warp knitting machine have been found particularly advantageous. Tricot stitching is especially suitable, both in ease and speed of production and in the efficiency of the final product. The tricot knit provides many large knots surrounding large holes, which results in an effective distribution of catalyst or getter throughout the fabric, while permitting the reaction gases to pass through the fabric without back pressure problems.

Raschel or jacquard knitting techniques are also useful, as they allow greater density and unit weight, and can produce a gauze of greater depth.

The knitted textiles of the invention can also be made in any desired size, based on the capacity of existing knitting machines and on the catalyst and getter support sizes commonly used in the industry. When a rotary knitting machine is used, tubes of up to 30 inches diameter can be made, with a 10 inch diameter being the most common. The knitted tube can be flattened to provide a two-layer catalyst or getter that is up to 47 inches wide, or it can be slit to provide a single-layer catalyst or getter that is up to 94 inches wide, or two

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single-layer pieces that are each up to 47 inches wide. When a warp knitting machine is used, a single-layer textile of up to 200 inches wide can be made.

Of the two types of knitting machine proposed for the purpose of knitting gauze, namely the rotary type and the warp type, the warp machine is currently preferred. This is because the rotary machine produces a product which has to be further processed (e.g. by slitting or flattening) to produce a flat gauze. These additional manufacturing operations increase production time and production cost. More seriously, existing rotary knitting machines are of a size which is incapable of producing a seamless gauze large enough to suit all reactors. As mentioned above, the largest known rotary machine can produce a tubular product of 30" (0.762 m) diameter which, when slit and flattened out, forms a gauze approximately 94" (2.39 m) wide. In contrast, existing warp knitting machines are capable of producing a seamless flat gauze up to 200" (5.08 m) wide - enough for the largest known reactors. Also, warp knitting machines can produce a variety of knits, stitches or mesh types including jacquard, raschel and tricot. As mentioned above, these stitches allow a large amount of catalytic or getter material to be incorporated into a given catalytic or catchment layer, but without restricting the interstices of the mesh so far as to create an excessive pressure drop when the mesh is in use.

It is envisaged that the invention will give particular benefit where the knitted wires are of intrinsically catalytic material. This is because certain reactions, particularly the oxidation of ammonia, cause a substantial loss of catalytic material through volatilisation. Thus, if the catalyst is not intrinsically catalytic but is merely composed of a catalytic layer coated onto a non-catalytic substance (e.g. a platinum-coated base metal wire), this loss will, quite quickly, erode the coating until the non-catalytic surface of the substrate is exposed. Clearly, the reaction will then cease. On the

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other hand, catalysts of intrinsically catalytic material will continue to present a catalytic surface during erosion, thereby sustaining the reaction until, eventually, they erode away entirely. In other words, intrinsically catalytic material maximises reactive depth so that, for example, a Rh-Pt wire of 0.003" (0.0762 mm) diameter provides an effective depth of reactive or catalytic material of 0.0015" (0.0381 mm). Providing a Rh-Pt coating of similar depth on an autocatalyst or even on a wire would be inefficient and costly.

The nature of the catalytic wires themselves depends upon the application envisaged for the catalyst. Usually, the wires will be of platinum group metal (pgm) such as platinum or palladium, or of a pgm alloy with total pgm content in excess of 90%. Such a composition can be used in many reactions, for example: the oxidation of ammonia to form oxides of nitrogen or to form hydrogen cyanide; the oxidation of carbonaceous material such as carbon monoxide, hydrocarbons or polychlorinated biphenyl; and the reduction of oxides of nitrogen or of oxides of sulphur. In other applications such as the oxidation of methanol, the wires will be of silver or of a silver alloy with silver content in excess of 75%.

Experience teaches that, in general, pgm alloys containing platinum or palladium in excess of 80% enjoy advantageous properties. Examples are 90% platinum with 10% rhodium, 90% platinum with 5% rhodium and 5% palladium, and 85% platinum with the remainder palladium and rhodium. It has also been found that a pgm alloy of 60% platinum with the remainder palladium and rhodium is effective.

Similarly, the knitted wires can be of any suitable size, examples being in the range 0.05 mm to 0.5 mm, and preferably in the range 0.055 mm to 0.1 mm. The weight of the wire can be in the range of, say, 200 to 1000 grams per metre.

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Of course, any of the wires outlined above can be used together by, for example, being knitted together or being incorporated into different gauzes installed contiguously to form a tailored pack (either with or without a separating inert gauze, felt pad or knitted screen between layers of the pack). Also, knitted gauzes formed from any of the above wires can be encapsulated by a catalytic mesh to form a cartridge that looks essentially similar to existing cartridges. Knitted gauzes can also be supported by an inert screen.

- 10 It is envisaged that knitting will be especially suitable for the production of catchment gauzes. Whilst any of the stitches disclosed herein may be used for catchment gauzes, jacquard knits in particular would be advantageous in view of their 'three-dimensionality'. In other words, each layer of jacquard knitted material has a marked thickness which means that post-reaction gases take longer to pass through the layer, thereby increasing its catchment performance. Jacquard knitted material may also improve the catalytic performance of catalytic layers, for the same reason.
- 20 The limitations of circular or rotary knitting machines in terms of lack of width tend to be less acute in the field of catchment gauzes. This is because, in some applications, catchment gauzes are hidden out of sight within a pack and therefore the presence of seams is relatively unimportant.
- 25 Indeed, it is possible for the tubular knitted product simply to be folded over and packed down to form a catchment layer. The advantages of circular or rotary knitting machines, such as speed and flexibility, can therefore be enjoyed under such circumstances without significant penalty.
- 30 A further potential benefit of knitting stems from the fact that the characteristics of the wire (diameter, composition and so on) can be readily varied during knitting simply by substituting a new wire. This facilitates the production of tailored packs, in which the characteristics of the wire are

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tailored to suit the conditions (of material loss etc.) prevailing at different points through the pack. Thus, the layers of the tailored pack can be knitted in a continuous operation, even though each layer requires a different wire.

- 5 Another advantage of knitting is that catalyst packs can be produced to a desired thickness without having to form layers of gauzes or felts. This helps to reduce production costs and also minimises expensive installation time. The knitting process can be similar to that used in the manufacture of
10 lace, in which additional material is knitted on to a knitted or woven backing to produce regions of a desired thickness. Another way of thickening a layer is to produce a 'pile' similar to velvet or velour cloths.

A knitted layer may have non-uniform thickness so that, for
15 example, the central region of a layer is thicker than the outer region of that layer. Such an arrangement may be advantageous as it allows the residence time of gases passing through the layer to be tailored to suit a velocity gradient across the width of a reactor. For example, the velocity of
20 the gas stream is generally lower adjacent the walls of a reactor than towards its centre. Hence, the centre of a layer may be thickened so that the residence time is more nearly uniform across the layer. It is similarly possible to vary the thicknesses of the individual wires that make up the layer,
25 so that the catalytic effect varies across the layer.

A further possibility is to thicken the edge or edges of a layer to compensate for the edge erosion that is sometimes observed. At present, reinforcing patches are commonly used to restore and/or to reinforce the edges of a catalyst pack.

- 30 Of course, arrangements combining a thickened edge region and a thickened central region are also possible, as are arrangements combining a variable-thickness layer with variations in the thickness of the wires making up the layer.

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Embodiments and aspects of this invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Fig. 1. shows a partial cross-sectional view of a prior art
5 woven gauze useful in ammonia oxidation catalyst or getter systems;

Fig.2. shows a partial cross-sectional view of a single face knitted textile according to the invention, made on a single-bar warp knitting machine;

10 Fig.3. shows a partial cross-sectional view of a double face knitted textile according to the invention, made on a warp knitting machine;

Fig. 4. shows a knitted textile being made on a warp knitting machine with bearded needles that stitch in unison;

15 Fig. 5. shows a partial cross-sectional view of a preferred knitted textile having a tricot stitch, as made on a Mayer warp knitting machine; and

Fig.6. shows a partial cross-sectional view of a netting type stitch made on a two-bar Raschel knitting machine.

20 Knitted precious metal textiles according to the invention can be made from single or multiple strands of wire, each strand having a diameter of about 0.05 mm to 0.10 mm. Representative knitted textiles of the invention include those with wires having a diameter of 0.06 mm, 0.675 mm, 0.76 mm, 0.09 mm, and
25 combinations thereof. The wire can be made of any precious metal (this term including precious metal alloy). Particularly suitable catalyst results have been achieved with platinum wire, especially platinum alloys that contain more than 50 percent platinum. Representative alloys with rhodium and

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palladium are shown in Table 1.

TABLE I

Composition of Wires Used in Knitted Metal Textiles

	<u>#</u>	<u>Platinum</u>	<u>Rhodium</u>	<u>Palladium</u>
5	1	95%	5%	
	2	90%	5%	5%
	3	90%	10%	
	4	92%	8%	
	5	92%	3.5%	4.5%
10	6	90-95%	2.5%	2.5%
	7	97%	3%	
	8	75%	4%	21%

When a textile for use in a getter system is desired, it has been found that wires made of palladium and palladium alloys are preferred, especially alloys that contain more than 50% palladium.

Certain knitting patterns are especially advantageous, including jacquard, raschel and tricot designs. These patterns, which contain a large number of large knots surrounding large holes, permit a large quantity of wire to be used in a small space, without closing up the holes and causing back pressure problems. Thus, in comparison with conventional woven gauzes, more catalyst or getter material can be used in the same space. This results in improved reaction efficiency, without blocking the flow of reaction gases.

The structure of a conventional woven gauze is shown in Fig.1. These gauzes are extremely simple, and are made of overlapping perpendicular strands (a,b) which lay next to each other, but which are not looped, stitched, knotted, or otherwise bound

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to each other. Woven material is quite different ven from a relatively simple single face knitted fabric made on a single bar warp knitting machine, as shown for example in Fig 2. A double face warp knit (having loops in two directions) further illustrates the differences in structure and complexity between prior art woven gauzes and the knitted precious metal textiles of the invention, as shown in Fig.3. Indeed, given the relatively fragile nature of precious metal wires and their high costs, it was thought prior to this invention that knitted precious metal catalysts and getter systems could not be suitably made. It was believed that the complexity of the knit compared to weaving would result in breakage, uneven results, and difficult problems of control that would render knitting impractical, and more costly and time consuming than weaving. However, it has now been discovered that precious metal wires can be knitted according to the invention into textiles that are superior in strength and construction to conventional woven gauzes. Furthermore, it has been discovered that knitted textiles can be made much faster than woven gauzes, without breakage and quality control problems.

According to the invention, any conventional knitting machine can be adapted to produce the textiles of the invention, including straight knitting machines, circular or rotary knitting machines and warp knitting machines. Multiple needle machines are preferred, so that large textiles can be rapidly made, and warp knitting machines have been found to produce especially advantageous results. Fig. 4 illustrates a knitted precious metal textile being made according to the invention on a Mayer warp knitting machine with latched bearded needles.

In addition to separate catalyst and getter textiles, the invention also contemplates "self-gettering" catalyst textiles, in which a catalyst material and a gettering material are knitted into a single composite textile. For example, catalyst strands comprising platinum as the predominant material can be knitted with getter strands

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comprising palladium as the predominant material, to provide an integral textile material that both catalyses ammonia oxidation reactions and immediately recaptures volatile catalyst material (such as platinum) which might otherwise be lost. Thus, one embodiment of the invention contemplates a new material that would permit a single textile to serve two purposes. With such a textile, conventionally separate downstream getter gauzes would no longer be needed. According to an aspect of the invention, metal losses can be reduced at or very near the source of loss by knitting the catalyst and entrapment systems into one textile. As just one example of how this can be done, a single continuous textile can be knitted, which has alternating sections of predetermined length of catalyst and getter material, the final textile can then be folded into a pack, comprising adjacent alternating layers of catalyst and getter as desired. The resulting self-gettering catalyst can then be conveniently supplied as a unitary cartridge.

The invention is also suitable for knitting tailored catalyst packs, which provide reduced weight of the same efficiency by using tailored overlapping shapes.

In another embodiment, a textile can be knitted using strands of different thickness along the length of the material - a result which cannot be achieved by conventional weaving, since thread sizes on a loom cannot be readily changed anywhere in the textile as they can in a knitting process. Thus one advantageous product according to the invention, uses thinner wires at the top and thicker wires at the bottom, to provide a knitted precious metal textile with a strong pyramid-type infrastructure. This thickness profile can also be reversed or otherwise varied to produce a pack whose wire thickness at a given point in the pack is tailored to suit the metal loss rate expected to that point in the pack.

To make the knitted precious metal textiles of the invention,

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it has been necessary to overcome certain problems not encountered in conventional weaving processes, and not encountered in traditional fabric knitting processes. Unlike weaving, which does not loop strands of wire and does not use knots and binding points, the knitting process draws strands of wire into sharp loops, through which needles carrying other strands are passed, to form a looped stitch. Initially, attempts to knit precious metals were unsuccessful, due to constant breakage of the wire thread and jamming and seizing problems with the various knitting machines that were tried. The resulting textile products were uneven and unsatisfactory. After many experiments, and with much trial and error, it was discovered that knitted precious metal textiles can be made using precious metal alloys of platinum, rhodium and/or palladium, in thicknesses ranging from 0.05 to 0.10 mm. This can be achieved either by lubricating the wire with a lubricant that does not interfere with the knitting machine, or by using a transitory feed thread to guide the wires. Where a transitory feed thread is used, it is advantageous for the thread to be of copper alloy: this can be etched away after knitting.

In some cases, it is also necessary to operate the knitting machine at slower speeds than are commonly used for knitting fabrics or non-precious metals. Suitable lubricants include spray starch and spray wax. Even at slower speeds, a lubricated metal textile can be knitted as much as ten times faster than conventional catalyst gauzes can be woven on a loom.

Knitting machines using independently moving needles, or latched needles which move in unison can be used, and straight, circular, or warp knitting machines are suitable, though warp knitting machines are preferred. Knitted metal textiles of the invention can also be made with loops which follow either the length or width of the fabric. In warp knitting machines, a large quantity of parallel threads

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running lengthwise are fed to one or more needle bars, with collectively moving needles. These threads are laid around the needles by loopovers to simultaneously form stitches across the width of the material. Single face and double face knitted fabric can be used, although single face embodiments such as tricot are easier to produce.

The invention is further described with reference to a number of examples. It is to be understood that these examples are illustrative, and do not limit the scope of the appended claims.

Example 1

A knitted textile according to the invention was made on a Mayer warp knitting machine, which permits a standard knitting matrix of about 40 x 40 wires. See, for example, Figure 4 of the drawings. The machine can be modified, however, to produce other matrices as desired. Depending on the chosen stitch, a square, oblong, or other lattice can be made. Mayer machines most suitable for knitted catalyst and getter textiles are available to knit in widths of 84 inches and 210 inches, at speeds of about 50 to 100 feet per hour. The preferred textile made on the Mayer machine, according to the invention, is a tricot pattern, as shown in Fig.5.

In one embodiment found to be suitable, wire having a diameter of .003 inches (0.076 mm) and a composition of 90% Pt 5% Rh - 5% Pd was knitted on an 84 inch machine into a textile 36 inches long. An acceptable product with a fine uniform weave was achieved by lubricating the wire with spray starch, and by feeding the wire through tension controllers in conjunction with the actual knitting. The best results were achieved using double bar operation, which produced a strong, durable and flexible knit, although single bar operation is somewhat faster and easier to manage.

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One sample of warp knit tricot material 11 x 13 inches long, weighed 53.6 g and had a density of 583 g/m², which is suitable for catalyst and getter applications.

Example 2

- 5 As shown in Fig.6, a Raschel knitting machine can be used to knit a netting-type pattern, using two-bar construction.

Example 3

- A knitted precious metal textile was made on a Tritex circular or rotary knitting machine, which produces a closed tube or
10 sock of material having a netting-like appearance. The Tritex machine produces a tube with a maximum diameter of 30 inches, which can be slit to form a textile product that is either 94 inches in one layer, or 47 inches when doubled. The Tritex machine produces a maximum knitting matrix of 25 x 30 wires,
15 which results in a relatively open knit in the final product. The Tritex textile was made of wires having a diameter of 0.003 inches, and a composition of 10% Rh-Pt. Using a 30 inch machine, the output is about 33 feet per hour.

Example 4

- 20 A knitted metal textile was made on a Lamb circular knitting machine. In this embodiment, using a 10 inch machine, it was necessary to run the precious metal wire with a polyester lead thread, to avoid snagging and breakage of the wire during loop formation. Multiple strands of wire can be knitted
25 simultaneously in this way. Other lead threads, such as nylon, cotton, rayon or the like, can also be used. The lead thread can be dissolved or burned away prior to use, or during final flame activation of the material, or even with the first on-site use. A tubular sample of this textile that was 1 1/4 inches
30 wide and 15 1/4 inches long weighed 14.5 g, and had a density of 418 g/m². The density can be altered by increasing or

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decreasing the number of needles, or by adding or subtracting strands of wire.

CLAIMS

1. A knitted textile product made of precious metal wires.
2. A knitted textile product according to claim 1, comprising jacquard, raschel or tricot stitches, or any combination
5 thereof.
3. A knitted textile product according to claim 1 or claim 2, whose thickness is non-uniform.
4. A knitted textile product according to claim 3, whose thickness increases moving inwardly away from its edges.
- 10 5. A knitted textile product according to claim 3 or claim 4, whose edge regions are thickened.
6. A knitted textile product according to any preceding claim, having non-parallel side edges when uncut.
7. A knitted textile product according to any preceding claim,
15 whose wire density is non-uniform.
8. A knitted textile product according to any preceding claim, whose wire characteristics are non-uniform.
9. A knitted textile product according to claim 8, wherein the differing characteristics include wire diameter or wire
20 composition.
10. A knitted textile product according to any preceding claim, comprising catalyst wires and getter wires.
11. A knitted textile product according to claim 10, wherein the catalyst wires are predominantly platinum and the getter
25 wires are predominantly palladium.

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12. A knitted textile product according to any preceding claim, wherein the precious metal wires are of intrinsically catalytic material.
13. The use of a knitted textile product defined in any preceding claim, as a catalyst or as a getter, or as a self-gettering catalyst.
14. Any substance produced by the use of a knitted textile product defined in any of claims 1 to 12, as a catalyst or as a getter, or as self-gettering catalyst.
- 15 15. The use of a knitted textile product defined in any of claims 1 to 12, in the synthesis of hydrogen cyanide from ammonia and methane.
16. Hydrogen cyanide synthesised from ammonia and methane by use of a knitted textile product as defined in any of claims 1 to 12.
17. A catalyst pack containing a plurality of layers, wherein at least one of the layers is a knitted textile product according to any of claims 1 to 12.
18. A catalyst pack according to claim 17, wherein the layers are formed by a continuous knitting operation.
19. A catalyst pack according to claim 18, wherein the layers are produced by folding a single knitted textile product.
20. A catalyst pack according to any of claims 17 to 19, wherein the wire characteristics vary from one layer to another.
21. A catalyst pack containing at least one concealed catalyst or catchment layer, the concealed catalyst or catchment layer comprising a precious metal knitted textile product produced

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on a rotary knitting machine.

22. A catalyst pack according to claim 21, wherein the concealed catalyst or catchment layer comprises a plurality of pieces of rotary knitted product joined together.

5 23. A catalyst pack according to claim 21 or claim 22, wherein the concealed catalyst or catchment layer is formed by folding over and packing down the knitted textile product.

24. A method of manufacturing a precious metal textile, comprising knitting together precious metal wires in a
10 knitting machine.

25. A method according to claim 24, comprising lubricating the precious metal wires before and/or during the knitting process.

26. A method according to claim 24 or claim 25, wherein the
15 knitting machine is a warp knitting machine.

27. A method according to any of claims 24 to 26, comprising varying the width of the knitted product emerging from the knitting machine, to produce an uncut knitted product having non-parallel side edges, such as a circle.

20 28. A method according to any of claims 24 to 27, comprising varying the thickness of the knitted product to produce a knitted product whose thickness is non-uniform.

29. A method according to any of claims 24 to 28, comprising varying the characteristics of the wires during the knitting
25 process.

30. A method according to any of claims 24 to 29, comprising varying the wire density of the knitted product by varying the number of wires fed to the knitting machine.

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31. A method of manufacturing a layered catalyst pack, comprising knitting the layers of the pack in a continuous operation and then folding the knitted product to form the layered pack.

- 5 32. A method according to claim 31, comprising varying the characteristics of the wires from one layer to another, thereby to produce a pack whose layers have different characteristics.

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FIG.1 PRIOR ART

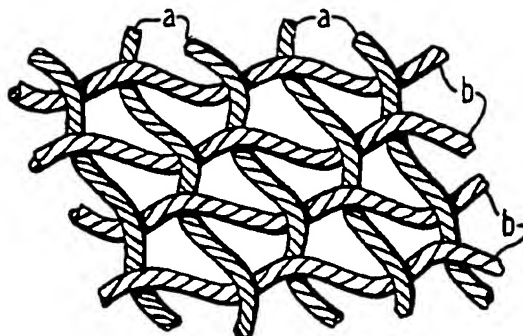
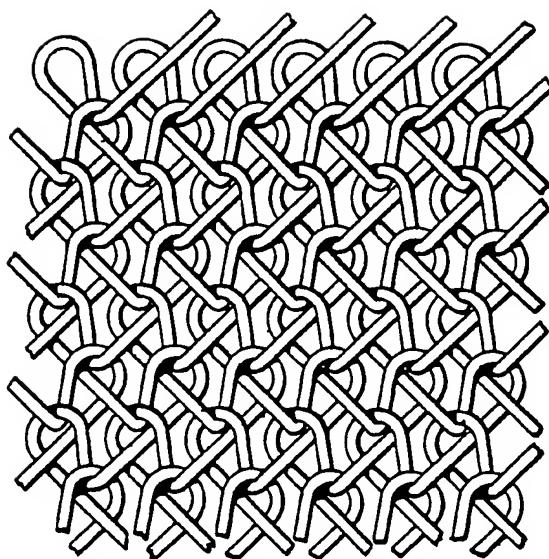


FIG.2



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FIG. 3

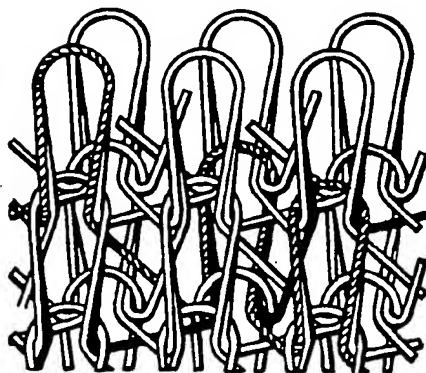
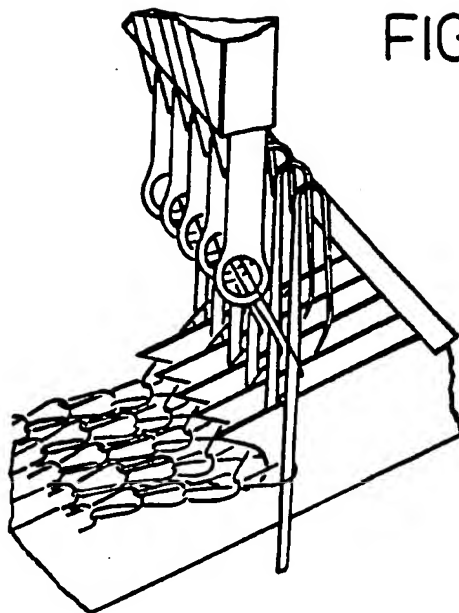


FIG. 4



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FIG.5

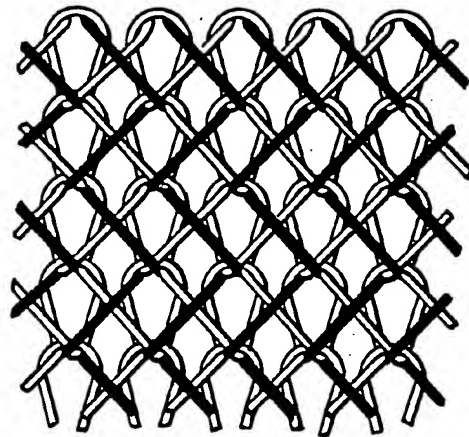
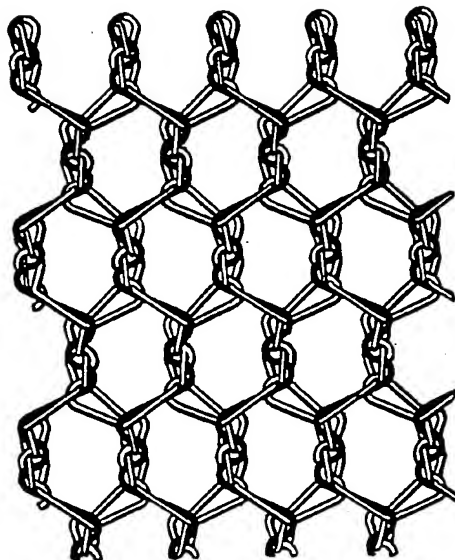


FIG.6

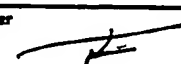


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INTERNATIONAL SEARCH REPORT

PCT/GB 91/01293

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B01J35/06; C01C3/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B01J ; C01C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 364 153 (JOHNSON MATTHEY) 18 Apr11 1990	1,2, 12-14,24 15-17
Y	see page 6; claims 1-11 see page 4; example 1 ---	
Y	DE,C,935 428 (ROHM & HAAS) 20 October 1956 see page 2, line 43 - line 46 ---	15,16
Y	EP,A,0 275 681 (JOHNSON MATTHEY) 27 July 1988 see figure 1 see page 2, line 33 - line 37 see page 6; claims 1-13 ---	17
A	FR,A,771 524 (COMPTOIR GENERAL DES METAUX PRECIEUX) 10 October 1934 ---	
A	GB,A,2 062 486 (JOHNSON MATTHEY) 28 May 1981 ---	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14 NOVEMBER 1991	27 NOV 1991 ¹	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	THION M.A. 	

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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9101293
SA 50320

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The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82